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# PYROTECHNIC RESEARCH AT DOFL PART II. PYROTECHNIC DELAYS

Raymond H. Comyn

15 February 1962



**DIAMOND ORDNANCE FUZE LABORATORIES**  
**ORDNANCE CORPS • DEPARTMENT OF THE ARMY**

WASHINGTON 25, D. C.

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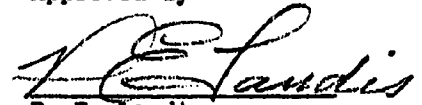
15 February 1962

**PYROTECHNIC RESEARCH AT DOFL**

**Part II. Pyrotechnic Delays**

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FOR THE COMMANDER:  
Approved by

  
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## ABSTRACT

This paper reviews pyrotechnic delay investigations at DOFL during the past several years. These studies include T2, T5, and T6 delay elements; delay ignition; fast and slow burning compositions; storage stability of mixtures; methods for measuring gas and heat evolved by these compositions; mixing procedures; and new methods for employing pyrotechnic mixtures for producing time delays.

The burning time dispersions, over the temperature range  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ , will be at least  $\pm 12$  percent under optimum conditions for delays burning within 20 sec and may be twice this value for longer delays or when conditions are less favorable. The new methods suggested for employing pyro mixes in time delays appear to offer no advantages unless used for very specialized applications.

The present compositions appear to be satisfactory for current DOFL requirements and no further investigations are recommended.

## 1. INTRODUCTION

This is the second and final report on Pyrotechnic Research at DOFL. The first report<sup>(1)\*</sup> reviewed DOFL investigations of pyrotechnic heat sources for Ordnance application. This paper deals with the use of pyrotechnic mixtures for producing controlled time delays. Part of these investigations were directed toward the development of specific end items and were financed by the appropriate Ordnance programs. However, a large part of the later studies were financed by the AEC and were directed toward the requirements of the Sandia Corp, an AEC contractor.

Pyrotechnic delay elements are used for producing controlled time delays<sup>(2,3,4,5,6,7,8)</sup> varying from 10 ms to over 100 sec in a number of Ordnance applications. These devices may be initiated by flame, by mechanical energy, or by low energy electric primers, and once initiated do not require external power for their operation. They may be contained in a small volume; they operate reliably at ambient temperatures between  $-100^{\circ}\text{F}$  and  $+165^{\circ}\text{F}$ , and they can withstand impacts in excess of 100,000 g while burning. However, these delay elements can operate only at pre-determined functioning times that cannot be adjusted after manufacture. Also, they are not very accurate. Under the best conditions, 95 percent of the burning times of a lot of delay elements, tested over the ambient temperature range  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ , will fall within  $\pm 12$  percent of a median value. Very often, the burning time dispersions of manufactured lots are higher than this and may be as high as  $\pm 30$  percent under unusual conditions.

\* Superscript numbers within parentheses refer to references at the end of this report.

The majority of the delay elements are prepared by pressing the dry delay mixture into columns at loading pressures of 30,000 psi or higher. The mixture starts burning at one end of the column at the start of the delay period, burns down the column and finally ignites the next element in the fuze train. The fast burning mixtures used in millisecond delays are initiated readily by flame, by electric primers, and by stab or percussion primers. However, the slow burning delay compositions do not ignite easily and a small amount of a fast burning gasless mixture must be pressed on top of the delay composition to transfer initiation from the primer to the delay column. Similarly, igniter compositions often are used to transfer ignition from the output end of the delay column to detonators or propellants. The latter have been used to move electric switches by gas pressure at the end of the delay period.

The gasless delay compositions generally are used for pyrotechnic delays. These are physical mixtures of one or more powdered metals and one or more oxidizing agents. Since the reaction of these mixtures produces a solid slag and comparatively little gas they usually are called "gasless mixtures." However, this gas, which is developed from impurities in the ingredients and surface moisture, is not insignificant and may be as much as 5-10 ml/g, at S.T.P. If this gas is confined in the delay column, the resulting pressure causes erratic burning times, but the pressure may be reduced easily by venting the delay column to the atmosphere or into very small internal expansion chambers.

Other methods have been considered<sup>(7,8,9,10,11,12)</sup> for employing pyrotechnic mixtures in timing devices. One of these uses flat pyrotechnic material<sup>(6,7,8)</sup> made of gasless mixtures and other chemicals similar to those used in heat source applications. Such a material could be made into spiral and other compact shapes that could not be manufactured using conventional dry powder loading techniques. In a second method<sup>(9,10,11,12)</sup> the gasless mixture is used to heat one end of a metal or ceramic rod. After a definite time lag the temperature at the opposite end of the rod would rise to a critical value and initiate an explosive, melt solder, or melt a salt that would conduct electrically in the molten state. A final method of employing pyrotechnics for timing uses a mixture of iron, boron, and potassium dichromate dispersed in a polysulfide binder<sup>(13)</sup>. While such delays are not gasless by any means they may be useful in devices where gas and flame can be tolerated. The burning rate of these compositions is not affected appreciably by external gas pressure and, therefore, the device may be used in rocket applications where it can be ignited directly from the rocket motor.

Gasless pyrotechnic mixtures may be used for producing controlled heat<sup>(1)</sup> in Ordnance devices as well as time delays. Many of the gasless compositions are used interchangeably as heat powders, delay igniters, and fast delays. Also, some of the methods developed for making and evaluating heat materials are applicable to delay applications.



Therefore, this discussion will include some techniques and methods useful for delay compositions although they may have been developed primarily for heat source application.

During the past several years an investigation of delay compositions and their applications has been continuing at DOFL. Part of this was directed toward specific Army Ordnance applications and part was conducted for the AEC and the Sandia Corporation(14). Since these investigations are being terminated at DOFL, this report is being prepared to summarize the work that has been completed and to consider the need for future work.

## 2. DELAY ELEMENTS WITH SHORT FUNCTIONING TIMES

The T2E1 delay elements (2,3,15,16,17,18) were developed at DOFL for use in the T709 and T771 mechanical bomb fuze. Originally, the delay mixtures and loading procedures were varied to produce five specified time delays: (1) instantaneous; (2) 0.010 sec; (3) 0.025 sec; (4) 0.120 sec; (5) 0.240 sec. Later, a 0.050-sec time delay was added to the series.

The T2E1 delay element is shown in figure 1. The original work was done using mixtures that had been blended by dry mixing techniques(2,3). Zirconium-iron oxide compositions were used to produce the 0.010- and 0.025-delay times, and zirconium-barium chromate compositions for the longer delay times. In later work, T2E1 delay elements were used to evaluate the reproducibility of mixtures for blending investigations (15,16,17,18). These data are shown in table I. The burning times of 20 units fired at room temperature were within  $39.56 \pm 1.76$  ms.\*

Table I. Burning Characteristics of Zr-BaCrO<sub>4</sub> Mixtures\*\*

BaCrO <sub>4</sub> Lot No.	130	144	313	314	325	334	335
Zirconium Lot No.	706-9	706-9	706-9	706-9	706-9	706-9	706-9
Cal/g	445.6	447.3	444.5	445.4	443.5	446.5	444.9
Burning Time (ms)	38.73	40.61	40.19	39.50	39.56	39.97	40.15

\*Calculated for 95% of all future observations at a 90% confidence level.

\*\*Data reproduced from reference 15.

It is believed that these data represent the optimum time dispersions that can be obtained with T2E1 delay elements at room temperature. The same percentage dispersions probably can be expected when the burning time is increased to 200 or 300 ms. Unfortunately, no tests were made at extreme ambient temperatures using T2E1 delay elements loaded with mixtures blended by the new wet blending techniques, and no estimate can be made of burning time dispersions to be expected over the military ambient temperature range. The T2E1 delay elements contain M42 percussion primers and must be initiated by mechanical action. It is recommended that M42G primers<sup>(23)</sup> be considered for future designs since they initiate pyrotechnic mixes more reliably than does the M42. It appears probable that the same mixtures could be initiated electrically in the same basic body design and would burn with low time dispersions. However, a few tests would be necessary to confirm this.

### 3. DELAY ELEMENTS WITH LONG FUNCTIONING TIME

Two delay elements have been designed at DOFL for use in the T788 tail bomb fuze to provide functioning delays after bomb impact. These are the T5E3 and T6E4 delay elements<sup>(4,5,19)</sup> with nominal times of 4.5 and 12.5 sec, respectively. The requirements for these devices included functioning after long storage, functioning over the ambient temperature range -65°F to +165°F, and functioning after multiple impact.

The latter test is particularly severe and is designed to duplicate conditions encountered by a delay when a bomb bounces after impact. In this test the delay element is mounted in a large steel ball and after 6 hr of temperature conditioning is dropped onto the first of four staggered steel plates spaced 12 ft apart vertically. The ball assembly is designed so that a firing pin is released and strikes the primer in the delay on the first impact.

The aluminum delay body shown in figure 2 is used for both the T5E3 and T6E4 delay elements, and in each case the delay body is loaded with DM-5 igniter<sup>(20)</sup> and DM-4 delay composition<sup>(21)</sup>. The composition of the latter is varied, following a specified procedure<sup>(21)</sup> to obtain the desired burning time.

Both the T5E3 and T6E4 delay elements are initiated with M42 percussion primers. Although the primer and delay mixtures produce relatively little gas while burning, it is sufficient to exert considerable pressure (above 100 psi) when confined in the delay body. Gas pressures of this magnitude accelerate the burning rate of "gasless delays" in an erratic manner<sup>(22)</sup> and must be reduced to values near atmospheric pressure when low burning time dispersions are required. In these delay elements a thin blowout disc ruptures and vents the delay column to the atmosphere when the primer fires. Unfortunately, this method of venting the burning delay has not been completely successful. A far better method is to use a MK 102 stab primer that explodes to some extent in both directions leaving a vent hole to the atmosphere after burning. However, the mechanical design of the fuze required a percussion primer and a M42 was chosen. Here again, an unfortunate choice was made since

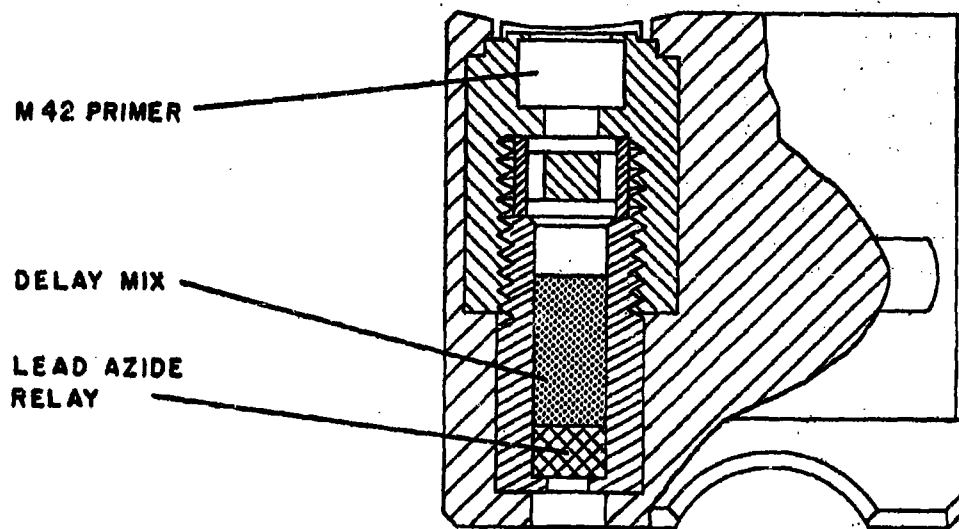


Figure 1. T2E1 Delay element.

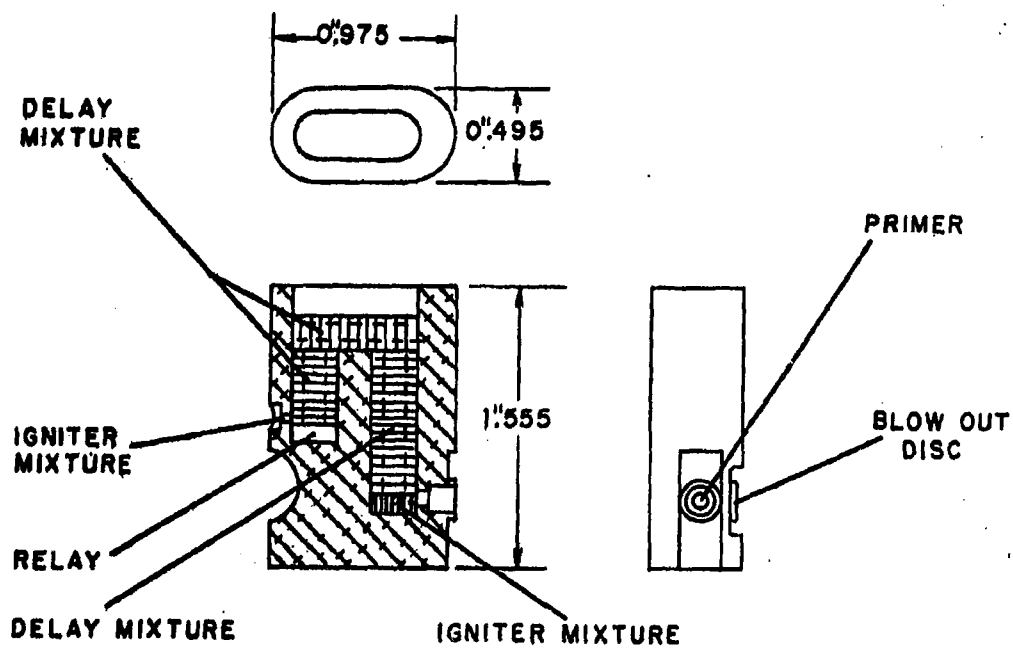


Figure 2. T5E3 and T6E4 Delay elements.

recent tests have shown<sup>(23)</sup> that the M42G primer ignites gasless mixtures far more uniformly than does the M42.

The T5 and T6 aluminum delay bodies were die-cast by the contractor using conventional die-cast procedures. However, later in the program these die-cast bodies were found to be porous and a silica treatment was used to seal the microscopic openings and to prevent moisture from seeping into the delay mixture during storage.

It is estimated that the functioning times\* of the T5E3 and the T6E4 delay elements should be within 4-5 and 11-14 sec, respectively. The functioning times measured during the design release tests had much wider limits. The proposed purchase descriptions based on these tests set limits of 3-9 sec for the T5E3 and 10-18 sec for the T6E4 with no defects permitted. Functioning times between 3-4 sec for the T5E3 and 10-11 sec for the T6E4 are permitted with an AQL (acceptable quality level) of 0.10. Functioning times between 8-9 sec for the T5E3 and 17-18 sec for the T6E4 are permitted with an AQL of 0.15. These delay times are based on multiple impact tests run on delay elements conditioned at -65°F, at +165°F, after 28 day MIL STD 301 T & H cycling, and after transportation and aircraft vibration.

The spread in actual burning times was much larger than had been estimated, and may have been partly due to the test procedures used. The very long burning times occurred only during the multiple impact tests and may be due to the primer being initiated at some time after the timing started. This could happen if the firing apparatus jammed and the primer was initiated on the second or third time the ball bounced on its way down the multiple impact apparatus. The timer always was started when the ball struck the first baffle.

The data for static tests in tables II and III below show that other factors than the multiple impact test contributed to excessive burning time dispersions. The erratic performance of the blowout discs may have caused part of the dispersions, since very short burning times often coincided with partial venting of the delay column. Another cause of dispersions may have been the increase of storage time of the delay elements during temperature and humidity cycling. An investigation<sup>(24)</sup> of the stability of the DM-4 delay mixtures showed that the burning time of the mixture changed very little during warm storage as long as the mixture was kept dry. It seems probable that leakage of water vapor through the delay body contributed to the increase of burning times during the temperature and humidity cycling.

\*Calculated for 95% of all future observations at a 90% confidence level.

Table II. Functioning Times (sec) of T6E4 Delay Elements in Static Tests

	$\bar{X}$	$\frac{60-80^{\circ}\text{F}}{\text{Std Dev}}$	N
No Accelerated Storage	12.74	0.441	21
2 wk Accelerated Storage	12.24	0.424	7
4 wk Accelerated Storage	12.53	0.330	7

Table III. Functioning Times (sec) of T5E4 Delay Elements in Static Tests

	$-65^{\circ}\text{F}$			$60-80^{\circ}\text{F}$			$165^{\circ}\text{F}$		
	$\bar{X}$	Std Dev	N	$\bar{X}$	Std Dev	N	$\bar{X}$	Std Dev	N
No Accelerated Storage	5.74	0.459	30	4.83	0.315	30	4.55	0.389	30
2 wk Accelerated Storage	--	--	--	5.36	0.608	10	--	--	--
4 wk Accelerated Storage	--	--	--	5.42	0.639	9	--	--	--

It is believed that future designs of this type should incorporate the following modifications: (1) ignition by stab primer with a baffle placed to protect the delay column from the primer blast; (2) use of a delay body made from solid metal, preferably brass, with adequate seals; (3) use of a straight delay column, if possible, to minimize loading and reduce sealing areas.

#### 4. DELAY IGNITION

The fast burning gasless mixtures used at DOFL for very short time delays can be ignited directly from primers, but the slower burning compositions generally require a fast burning gasless igniter to transfer ignition from the primer to the delay mixture. Since these igniter mixtures and fast burning delay mixtures are almost identical, the same primers may be used for initiating both fast and slow time delays.

The main factors that must be considered in igniting gasless delay mixtures are: (1) the delay column must not be disrupted; (2) initially, only the surface of the delay column should be ignited; (3) provision

should be made for reducing the pressure due to gases from the primer and delay. The first two factors may be partially controlled by placing a baffle between the primer and gasless mixture and by using a low brisance primer charge. However, even fairly violent primers such as the MK 102 stab primer are baffled adequately by the arrangement shown in figure 3. The MK 102 stab primer also allows direct venting to the fuze body or the outside atmosphere. Gasless mixtures do not ignite readily<sup>(22)</sup> when the absolute pressure is below 0.3 psia and, therefore, internal venting in a sealed delay element is recommended for low pressure applications.

Several methods are available for reducing the gas pressure in a delay element. If the delay operates inside a sealed fuze and if the small quantity of hot gas evolved by the primer and delay is not objectionable, the gases may be vented into space inside the fuze itself. Another method<sup>(6)</sup> is to load the delay mix into a delay body with a small OD and to vent the gases into an annular space between the delay body and the delay element casing. In general, it is advisable to use small quantities of priming mixtures that evolve little gas upon initiation. Electric initiators have been made<sup>(6)</sup> for gasless delay elements that use about 10 mg of lead styphnate and 10 mg of an igniter composition. Tests at these laboratories<sup>(26)</sup> have shown that initiators which contain 10 mg of a 425-cal/g zirconium, barium chromate, superfloss mixture pressed on 10 mg of milled lead styphnate ignite gasless compositions much more reliably, particularly at low ambient temperatures, than initiators containing only 35 mg of lead styphnate alone. The former initiators form a nonconductive ash after burning that prevents the initiators from draining energy from the fuzing system, as well as producing much less gas on initiation.

A mixture of zirconium, ferric oxide, and superfloss powders has been used for gasless igniters. This is known as A-1-A igniter when manufactured by the procedure outlined in reference 25. The same mixture prepared by a modified manufacturing procedure at DOFL has been called DM-3 or DM-5<sup>(20)</sup> to prevent ambiguity.

Although the zirconium-iron oxide-superfloss igniter generally ignites readily from standard primers and, in turn, ignites delay mixtures, it is not satisfactory in all respects; the manufacturing procedure is hazardous, complete specifications are not available, and this igniter has been shown<sup>(26)</sup> to contribute to dispersions in the burning times of delay compositions although the igniter itself burns very rapidly.

A new igniter made from zirconium, barium chromate, and superfloss has been developed at DOFL. The ingredients are completely specified<sup>(15,17)</sup> and include a nearly gasless barium chromate<sup>(1,15,27)</sup> developed for use in "gasless" mixtures. The igniter is called a split igniter<sup>(26)</sup> because it consists of separate mixtures. A small portion of about 40 mg next to the primer contains a high proportion of zirconium to enable it to ignite readily from the primer. A second portion of about 100 mg between the first portion and the delay mixture contains a much lower

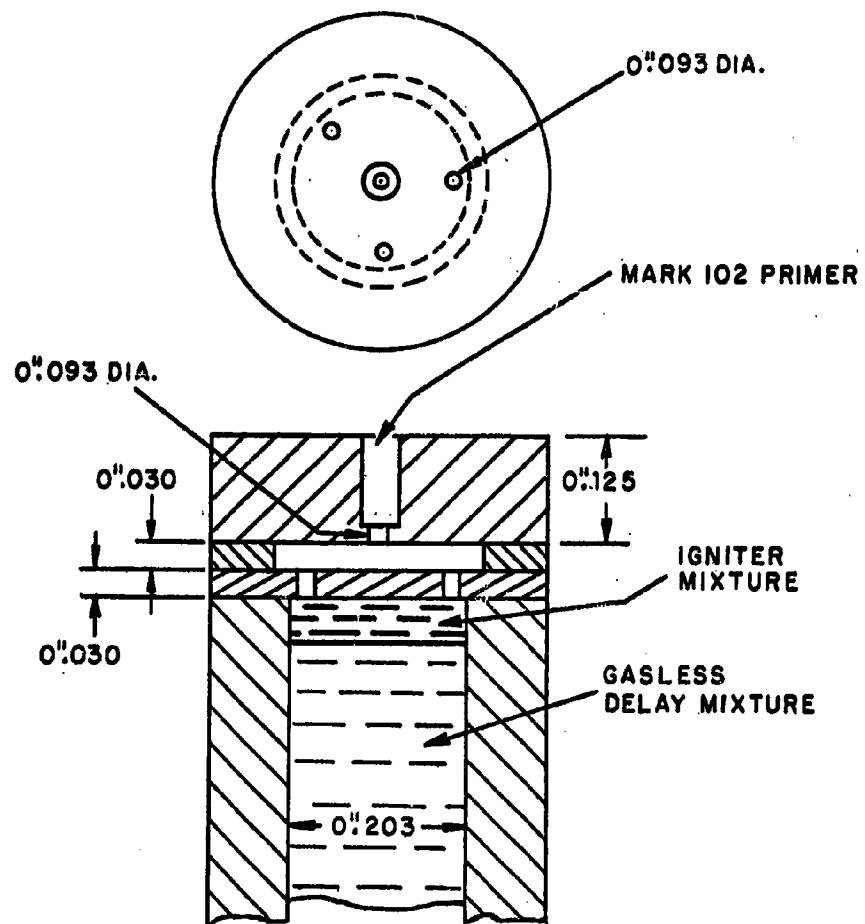


Figure 3. Ignition baffle.

proportion of zirconium. This second portion is designed to ignite the gasless mixture. Instructions for safe blending and testing of each of the two types of mixtures in the split igniter are included in the specifications<sup>(26)</sup>.

It has been found that mixtures which develop a relatively low number of calories per gram often ignite gasless mixtures more reliably than do compositions with a high heating value. This is true for both zirconium-iron oxide and zirconium-barium chromate mixtures. The ignition of gasless mixtures may be compared with melting solder with a soldering iron. In the latter case the hot iron must be firmly against the solder for a finite time. In the former case the igniter slag must be held against the gasless mixture after the igniter has reacted. Mixtures with high calorific values tend to react explosively and the slag becomes molten and draws away from the delay during combustion. Tests on the T6E4 delay elements have shown that units containing excessive quantities of igniter do not ignite reliably since in these cases the slag becomes molten and moves out of contact with the delay mixture.

This split igniter appears to be satisfactory for igniting slow burning delay mixtures and no further development is recommended.

#### 5. FAST BURNING DELAY MIXTURES

Two types of fast delay mixtures<sup>(2,3)</sup> have been used at DOFL for producing delays in the millisecond range. One of these was a mixture of zirconium-ferric oxide-superfloss and the other a mixture of zirconium and barium chromate. A gasless igniter study<sup>(26)</sup> has shown that the addition of about 10 percent Superfloss\* improves the loading characteristics of zirconium-barium chromate mixtures and its use in these delay mixtures is recommended in the future. Both of these compositions have been tested only in the T2E1 delay element, but they may be adapted readily to other designs.

During the initial investigation these mixtures were produced by dry blending techniques for the T2E1 program and were intended for producing time delays in bomb fuzes. In later studies the zirconium-barium chromate compositions were produced for a variety of investigations including heat powder<sup>(1)</sup>; zirconium specification<sup>(17,28)</sup> barium chromate specifications, <sup>(1,15,27,28)</sup> and mixing studies<sup>(18,16,18)</sup>. The mixtures were loaded into T2E1 delay elements and fired as a convenient method of measuring the burning rate of the compositions.

Although these investigations were not directed specifically toward developing fast delays, the information obtained in these studies is applicable to fast delay mixtures. For example, zirconium and barium chromate are completely specified<sup>(15,17,26,28)</sup> and the agglomerate method of

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\* A pure form of diatomaceous earth produced by the Johns-Manville Corp.



blending them is completely described in references<sup>(15,16,18)</sup>. Likewise, information obtained on the burning rate of heat powder mixtures is equally applicable to fast delay compositions.

The present fast burning mixtures appear to be satisfactory for known applications and no further development is recommended.

## 6. SLOW BURNING DELAY MIXTURES

Only three slow burning delay mixtures have been used or investigated at DOFL. These include (1) a mixture<sup>(29,30,31,32,33,34)</sup> of manganese, lead chromate, and barium chromate powders that had been called NOL-DI6<sup>(33)</sup>, manganese delay composition<sup>(34)</sup>, and DM-4<sup>(21)</sup>, depending on which specification is used; (2) a mixture of tungsten, barium chromate, potassium perchlorate, and Superfloss originally called UMNOL mixture<sup>(14,35)</sup> and later termed tungsten delay composition<sup>(36)</sup>; and (3) a mixture of iron, boron, and potassium dichromate dispersed in a polysulfide binder<sup>(13)</sup>. These investigations are discussed below.

### 6.1 Manganese Delay Compositions<sup>(24)</sup>

Mixtures of manganese, lead chromate, and barium chromate can be produced with controlled burning times varying from about 2 to 13.5 sec/in. The burning times of these compositions depend on the subsieve particle size of the manganese powder. Since the latter cannot be controlled closely, mixtures made with identical percentage compositions may not have the same burning times when made from different batches of manganese. To prepare mixtures with predetermined burning rates from a particular batch of manganese powder, it is necessary to vary the proportions of the mixture to compensate for changes in burning time due to the manganese size. Therefore, only the burning times and the method of preparing manganese mixtures are specified, and the percentage compositions are allowed to vary in a specified manner to obtain the desired burning times.

The effect on the burning time of variations in composition and loading has been studied previously. Generally, a standard pressure of 30,000 psi is used to load the dry mixtures in a column 0.203 in. in diameter. Smaller diameters may be used when the burning time is below 12 sec/in. The burning time of the mixtures loaded in comparatively small diameter columns is practically independent of column diameter unless the delay column is reduced to such a small size the delay mixture will not burn.

However, in an actual device two factors may have a pronounced effect on the burning time of a delay column, (1) the thermal quenching to which the mixture is subjected, and (2) the degree of confinement of the gases from the primer and delay column. These factors vary with the design of each device in which the delay is used and, therefore, the burning times of mixtures are determined by a specified procedure in which the delay mixtures burn at atmospheric pressure. Then a correlation may be

established between the standard burning time of a mixture and its burning time in the actual device.

The burning characteristics of various proportions of the manganese lead chromate, barium chromate mixtures have been established previously<sup>(31,32)</sup> along with the effect of delay body diameter and other loading variables. However, methods of manufacturing completely stable mixtures are not understood and DOFL investigations of the manganese mixtures have been concentrated in this area.

Some of the specifications<sup>(33,34)</sup> for manufacturing manganese delay mixtures require that the manganese powder be treated before it is mixed with the other ingredients. In this process, the manganese first is treated with an aqueous solution of potassium dichromate, dried, and then stirred in a solution of stearic acid in carbon tetrachloride. The excess stearic acid is removed with fresh carbon tetrachloride, leaving a film of chemisorbed stearic acid on the manganese.

Initial data indicated that the above procedure improved the stability of the manganese mixtures, and it was thought that the treatments inclosed each manganese particle in a protective envelope. However, there have been two objections to these treatments; (1) the manganese may react vigorously with water and potassium dichromate resulting in a reduced particle size that often produces mixes with too fast a burning time; and (2) the hydrous oxides of manganese formed during the treatment along with adsorbed stearic acid increase the gases evolved by the burning mixtures. Later work<sup>(24)</sup> at DOFL has shown that it is very doubtful that these procedures actually coat the manganese particles and improve the stability of the mixtures.

Studies have shown that some batches of manganese mixtures made with untreated manganese can be stored over water at +165°F without deterioration while other batches deteriorate rapidly. Mixtures that are completely stable require (1) barium chromate specified in reference 15, (2) reagent grade lead chromate produced from lead nitrate and chromic acid, and (3) manganese powder with a small crystallite size as determined by X-ray diffraction. It is not known if the crystallite size itself influences the stability of the manganese or if it is an indication of some unknown property.

The loose mixtures do not deteriorate under normal laboratory conditions and loaded mixtures do not deteriorate to an appreciable extent when stored dry at elevated temperatures (+165°F). For example, even mixtures made with large crystallite manganese, which will not burn after 3 days storage over water at +165°F, will increase their burning times only 5 percent during 8 wk dry storage at +165°F (table IV). For many purposes this increase is acceptable, and as long as the mixtures are properly sealed, no further difficulties may be expected. Adequate seals are necessary even when stable mixtures are used, since none of the mixtures will burn when wet. The main advantage of using completely stable delay mixtures is that they will tolerate the presence of small amounts of water vapor without deterioration and less rigorous sealing methods are

Table IV. Effect of Dry Storage on Burning Time of Manganese Delay Mixtures<sup>a</sup>

Delay Mixture Identification	Batch No. of Mn Used in Mix	Burning Time <sup>b</sup> (sec) After Indicated Exposure in Sealed Flasks at +165°F							
		Before Storage		1 Wk Storage		2 Wk Storage		4 Wk Storage	
		Av <sup>c</sup>	SD	Av <sup>c</sup>	SD	Av <sup>c</sup>	SD	Av <sup>c</sup>	SD
872	86	6.56	0.123	6.73	0.089	6.73	0.095	6.85	0.127
873	352	5.35	0.122	5.46	0.028	5.50	0.036	5.56	0.077
								6.86	0.117
								5.62	0.064

<sup>a</sup> 33% Mn, 30% BaCrO<sub>4</sub>, 37% PbCrO<sub>4</sub>.

<sup>b</sup> Mixtures loaded at 30,000 psi with 2-100 mg increments of DM-3 igniter in delay bodies 0.203 in. I.D., 0.500 in. O. D., 0.750 in. long.

<sup>c</sup> Average of ten tests.

necessary. Unless the small burning time increase of dry mixtures is objectionable, or present sealing methods are inadequate, it appears that no requirement exists for manganese delay mixtures that can be stored at +165°F over water. If such requirements are necessary, it is recommended that use of small crystallite manganese and oxide free grinding procedures be investigated.

## 6.2 Tungsten Delay Compositions (14,35,36)

The tungsten delay compositions (36), also known as UMNOL mixtures (35), were developed by a contractor for NOL, White Oak. Later the contractor began using tungsten delay mixtures in the 60-sec MC-835 delay switch that they developed and produced for the Sandia Corp. However, some difficulties were encountered in the delay switch production, and the AEC contractor requested DOFL to investigate causes and methods of eliminating or reducing the following: (1) a functioning time dispersion of about  $\pm 25$  percent over the ambient temperature range -65°F to +165°F; (2) a few short functioning times in each lot as much as 12 sec below the average; (3) a continuing decrease in functioning time as additional production lots were produced from the original batch of delay powder; and (4) a great deal of difficulty in making new batches of tungsten delay powder with a controlled burning time.

### 6.2.1 Time Dispersions

Although the 60-sec switch is not particularly complicated, its manufacture and loading require more time and personnel than were available at DOFL. Therefore, the majority of the DOFL tests used vented delay bodies 0.750 in. long, which were convenient to load and test. This was particularly necessary in view of the very low frequency of short and "instantaneous" burning times found in some lots of powder and the consequent large number of tests that were required. Since the lowest time dispersions are obtained with short vented delay columns, these tests were made under optimum conditions. Later tests were made in longer columns and in the MC-835 hardware.

The best results (37) were obtained with delay and split igniter mixtures prepared at DOFL, and loaded and fired in fully vented delay bodies 3/4 in. long. In one typical test, table V, col 1 and 2, 99 percent of the burning times calculated at a 90 percent confidence level were within  $18.97 \pm 2.19$  sec, or within  $\pm 11.52$  percent. In a second typical test, the burning times, Table V, col 3 and 4, calculated for the same limits, were within  $18.29 \pm 1.70$  sec, or  $\pm 9.30$  percent. However, the time dispersions increased as longer delay columns were used. A similar mix was loaded in the MC-835 switch hardware and fired fully vented over the same ambient temperature range (table V, col 5 and 6). Here, the functioning times, calculated in the same manner, were within  $53.33 \pm 12.95$  sec, or  $\pm 24.17$  percent.

One characteristic of the tungsten compositions that has caused much difficulty both at DOFL and in delay switch production is the

Table V. Performance of Tungsten Compositions

Col	Mix Ident	Test Temp (°F)	No. of Tests	$\bar{X}$ (sec)	Actual Range		SD (sec)	Type of Igniter
					Min (sec)	Max (sec)		
1*	773	+165	20	17.66	17.08	18.06	0.26	Split 3/4 in. vented
2*	773	- 65	20	20.68	20.46	20.96	0.14	Split 3/4 in. vented
3*	858	+165	20	17.03	16.81	17.25	0.13	Split 3/4 in. vented
4*	858	- 65	20	19.55	19.22	19.71	0.13	Split 3/4 in. vented
5*	871	+165	10	46.20	44.20	48.20	1.47	Split MC-835 vented
6*	871	- 65	10	60.29	56.60	61.63	1.51	Split MC-835 vented
7*	773-1	70	20	18.49	16.44	18.92	0.55	A-1-A 3/4 in. vented
8*	773-2	70	20	19.23 <sup>b</sup>	40.01 <sup>a</sup>	19.93	0.34 <sup>b</sup>	A-1-A 3/4 in. vented
9*	773-3	70	20	18.25	11.87	19.66	1.58	A-1-A 3/4 in. vented
10*	768	70	20	16.70	12.51	18.89	1.69	A-1-A 3/4 in. vented
11*	768	70	20	18.45	17.59	18.84	0.31	Split 3/4 in. vented
12	UM Corp. + 65		30	52.17	50.01	54.05	0.97	Split MC-835 sealed
13	UM Corp. - 65		30	75.71	68.13	77.22	1.54	Split MC-835 sealed

\* Data from reference 37

<sup>a</sup> One unit fired in less than 10 ms<sup>b</sup> 10 ms not included

low incidence of unusual burning times that appear in some tests. This is illustrated in table V, col 7, 8, and 9. All the units were fully vented and initiated by S-67 squibs loosely held against metal baffles supporting the delay columns. Therefore, none of the short burning times that were found could be attributed to anything else than the delay or igniter mixture. As shown in the data discussed above, one test produced normal burning times; a second test produced very even times with one exception, but that exception was below 10 ms; and a third test produced very uneven results. Therefore, an unusually large number was required to evaluate each mixture to establish its burning time range with some degree of confidence.

The main factor that makes it difficult to control the burning times of these compositions is the very large change in burning time caused by a small change in composition. This has been discussed previously<sup>(38)</sup>. The burning rates of these compositions are controlled by the tungsten/barium chromate ratios since both the Superfloss and potassium perchlorate are held constant at 10 percent, and have very little effect on the burning rate. The data in figure 4 show that a change of only 2 percent (from 28 to 30 percent) in the proportions of tungsten changes the burning time from 42 to 30 sec/in. However, a number of tungsten lots tested at DOFL produce mixtures that will not burn beyond about 36 sec/in., and therefore, a shift of less than 1 percent in the tungsten content of one of these compositions burning at 33 sec/in. will produce duds. When the macroscopic proportions of a mixture are critical, the microscopic proportions must be equally well controlled, and any unevenness in mixing in any portion of a lot of delay powder may cause the failure of one small section of a loaded column.

Initially, the agglomerate mixing method<sup>(7,15,16,18,37)</sup> was used to blend<sup>(37)</sup> tungsten compositions using toluene, which appeared to be best suited for a mixing vehicle. Although the mixtures appeared well mixed by microscopic examination, the burning times were erratic. Subsequent tests with dry mixtures in a Simpson Muller mixer showed that long mixing periods appeared to contribute to erratic burning times. Later, it was shown that the A-1-A igniter used in these tests was responsible for part of the erratic burning times and it was thought that a large sized potassium perchlorate used in these mixtures may have been responsible for some of the burning times below 10 ms. However, it was found that a 10-min mixing period under a dry atmosphere in a Simpson mixer produced the best mixtures and this method was adopted as standard.

It was found that the A-1-A used to ignite the delay penetrated the column<sup>(26)</sup> and ignited it below its surface. A split igniter was developed<sup>(26)</sup> to eliminate this, as discussed in section 4. The efficiency of the split igniter in reducing time dispersions in fully vented columns is shown in table V, col 10 and 11. However, this reduction in dispersions disappeared when it was used to ignite tungsten compositions loaded in the MC-835 hardware<sup>(37)</sup>. Sixty MC-835 delays were loaded at a contractor's facility with a production tungsten mix and split igniter.

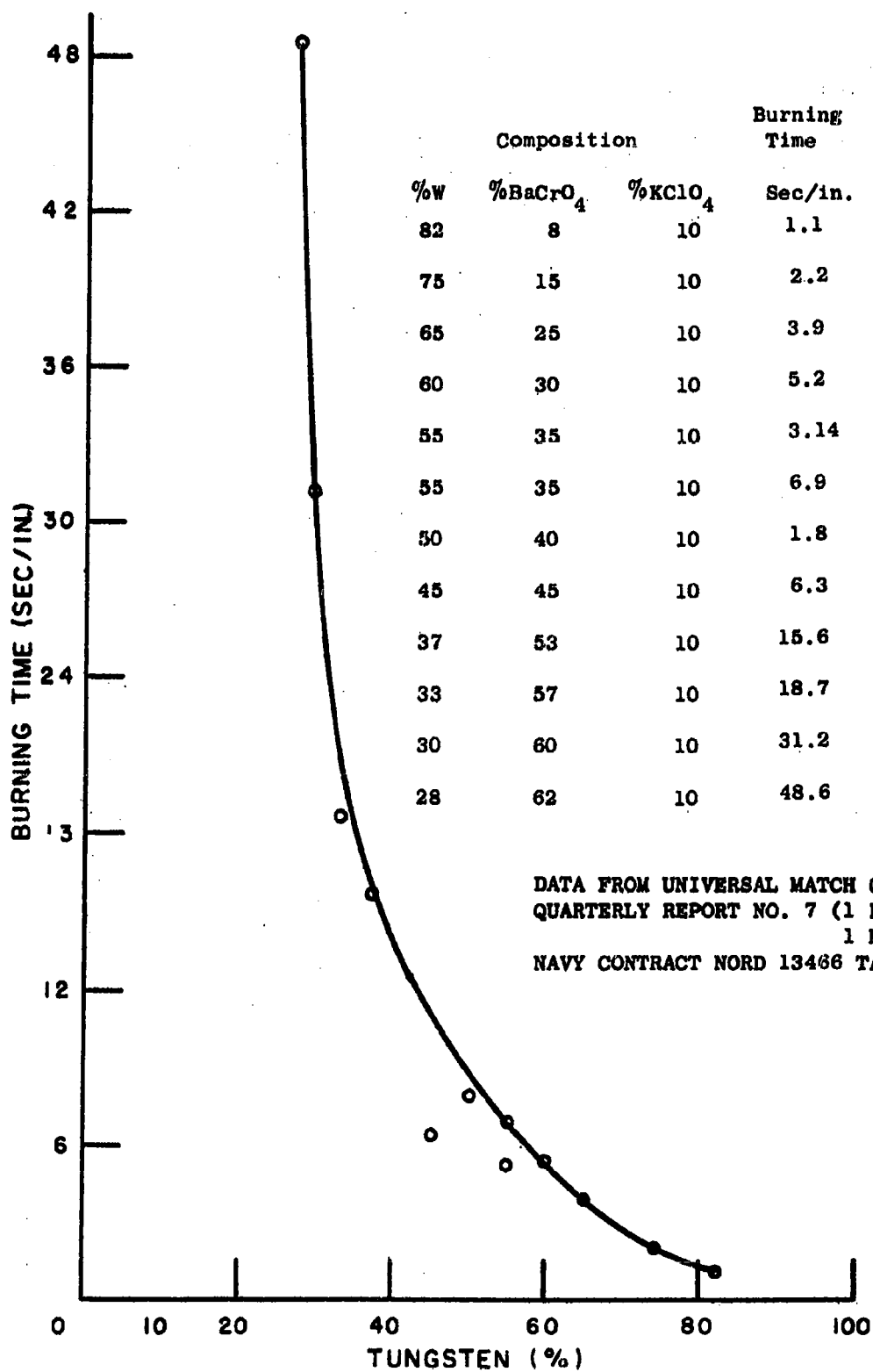


Figure 4. Composition versus burning times of tungsten compositions.

These units were fired fully sealed at  $-65^{\circ}\text{F}$  and  $+165^{\circ}\text{F}$  as shown in table V, col 12 and 13. The burning times of 99 percent of these units, calculated at a 90 percent confidence level, were within  $64.85 \pm 15.74$  sec ( $\pm 24.28$  percent). Later, twenty MC-835 delays were loaded with a tungsten mixture and split igniter at DOFL and fired at  $-65^{\circ}\text{F}$  and  $+165^{\circ}\text{F}$ . These burning times, calculated for the same limits, were within  $53.33 \pm 12.95$  sec ( $\pm 24.17$  percent).

The data in reference 39 showed that burning time dispersions over the ambient temperature range  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$  could be reduced by increasing the mass of the delay bodies. However, it was found<sup>(40)</sup> that the mass of the delay bodies did not affect the burning time dispersion of tungsten mixtures at  $+165^{\circ}\text{F}$ ; and that the unusually short burning times found in testing lots of tungsten powder at  $+165^{\circ}\text{F}$  could not be eliminated by increasing the mass of the delay bodies. This same study showed that the mass of the delay body affects the delay time by reducing the delay body temperature and the heat transferred to the unburned portion of the mixture. Apparently, heat removed from the reaction zone does not cool the reaction and affect the reaction time. Tests showed that the burning times of mixtures loaded in brass, aluminum, and ceramic bodies  $3/4$  in. long were not significantly different. However, there was a significant difference between the burning times of the same mixture loaded in 2-in. ceramic and 2-in. metal bodies. The burning time was much slower in the ceramic bodies indicating that the preheating of the unburned portion of the delay column was more important than the loss of heat from the reaction zone.

Preliminary tests<sup>(40)</sup> showed that the dispersion over the temperature range  $+70^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$  could be reduced markedly by burning the delay mixtures in a loaded column 0.156 in. in diameter, though, of course, the delay mixtures would not burn in such a small column at  $-65^{\circ}\text{F}$ . Numerous attempts were made to preheat the delay bodies from  $-65^{\circ}\text{F}$  to room temperature with heat powder or fast burning delay mixes. However, in all cases the tungsten mix either failed to ignite at low ambient temperatures or if it did ignite, the same test assembly would burn erratically at  $+165^{\circ}\text{F}$ . Additional tests were made to test the possibility of burning manganese compositions in similar small preheated columns. In this case, the objective was to produce a long delay column in a small space. However, these tests were equally unsuccessful.

It was concluded that the dispersions in tungsten compositions probably are a function of delay column length and cannot be avoided.

The burning of tungsten mixtures loaded in long columns usually is accompanied by very distinct gurgling and popping sounds that apparently are due to the generation of gas. Several precautions were taken to reduce the possibility of gas generation including the use of almost gasless barium chromate and thorough drying of the ingredients as well as the completed mixtures. It is believed that oxygen may result from the decomposition of the potassium perchlorate in the burning mixture and move



through the delay column. However, the function of the potassium perchlorate in the mixture is not understood. References 35, 37, and 38 have shown that the tungsten, barium chromate, and Superfloss powders will not react unless some potassium perchlorate is present. However, the addition of additional potassium perchlorate has no effect on the burning rate of the mixture until it is increased to the point where the mixture will not ignite. It is evident that the function of the potassium perchlorate is different from its usual one of an oxidizing agent and may be some type of catalysis. A few tests were made at DOFL to find a nongassing substitute for the potassium perchlorate but none was successful.

#### 6.2.2 Specifications

It was found that the proportions (10 percent) of potassium perchlorate and Superfloss generally used are satisfactory and that the proportions of tungsten and barium chromate depend on the burning time desired and the size distribution of the tungsten.

In general, as the tungsten/barium chromate ratio is reduced, the burning time decreases until the mixture will not burn. This maximum burning time changes with the size distribution of the particular lot of tungsten that is used. When the tungsten size is small, the maximum burning time may be only 17-18 sec/in.<sup>(37)</sup> Unfortunately, the methods available for measuring the tungsten size are not completely accurate, and it is difficult to predict the burning properties of mixes from measurements of the size of tungsten powder. This would be expected from consideration of the steep slope of the burning time-proportion curve (fig. 4) discussed previously. It is probable that the burning characteristics of a tungsten composition provide a more accurate criterion of the tungsten size than other methods usually used for size analyses. At any rate, the method now used for pretesting tungsten powder lots in actual mixes appears to be the most satisfactory procedure for determining the suitability of a tungsten lot for delay mixtures.

The barium chromate specifications<sup>(15)</sup> developed at DOFL for heat mixtures have been found to be satisfactory for use in tungsten delay compositions<sup>(37)</sup>; the Superfloss is a proprietary product available from the Johns Manville Corporation; and a pure form of potassium perchlorate is recommended. However, there is some evidence to show that very short burning times, below 10 ms, may occur when the size of the potassium perchlorate is too large and the size specifications in reference 37 should be followed. Two commercial air grinding procedures were found to produce potassium perchlorate with a satisfactory size distribution.

#### 6.2.3 Storage Stability

A study<sup>(39)</sup> showed that units loaded with tungsten composition can withstand +165°F for 4 wk with no appreciable change in burning time but they deteriorate when held at 240°F for 2 hr. Loose mixtures deteriorated when they were exposed to 100 percent rh and 165°F for 72 hr but only changed slightly when held at 80 percent rh and 165°F for 4 wk.

#### 6.2.4 Summary

Tests have shown that the burning time dispersions\* of tungsten delay compositions over the temperature range  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$  may be held below  $\pm 12$  percent when the mixtures are prepared carefully and fired in fully vented bodies about  $3/4$  in. long using split igniter. Here, the delay times were below 20 sec. As the length of the delay column and time are increased, the dispersions will rise to about  $\pm 25$  percent for a nominal 60-sec delay. Apparently, the tungsten delay compositions burn erratically in long delay columns. This phenomenon is believed to be due to (a) local concentrations of oxygen from the decomposition of potassium perchlorate; (b) preheating of the unburned delay by heat transferred through the delay body from the reaction zone. Preliminary tests showed that dispersions ( $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ ) could be reduced by using massive delay bodies, but this approach was eliminated when it was found that it did not prevent "shorts" at  $+165^{\circ}\text{F}$ . Later work has suggested that this approach should be re-examined using either massive delay bodies or ceramic liners to prevent the unburned delay from preheating.

The loaded delay mixes must be kept dry but if this is done the average delay times will fluctuate less than 4 percent during storage at  $+165^{\circ}\text{F}$ . Storage at  $240^{\circ}\text{F}$  for short periods has an adverse effect on the delay time.

At the present state of the art it may be difficult to obtain tungsten powder with the proper size to make long burning mixtures.

In view of the unusual characteristics of this composition that make control difficult, it is not recommended for general use in DOFL designs. However, if these compositions are required, the following recommendations are made:

(1) Investigate the possibility of reducing time dispersions in long columns loaded with tungsten composition by: (a) venting through openings along the column; (b) finding a nongassing substitute for potassium perchlorate; (c) using massive metal delay bodies or ceramic liners in the delay bodies to prevent heating of the unburned mixture.

(2) Investigate the possibility of producing tungsten powder with a satisfactory particle size by elutriation techniques. This would involve the use of a noncorrosive liquid and controlling its flow through a settling chamber to separate particles of varying sizes.

#### 6.3 Castable Delay Compositions

Castable delay compositions were formulated by the Thiokol

\* Calculated for 99% of all values at a 90% confidence level.

Chemical Corp on a DOFL development contract<sup>(13)</sup>. These compositions contained potassium dichromate with iron and boron powders dispersed in a polysulfide binder. Although these mixtures develop considerable quantities of gas during combustion, they have other characteristics that may make them particularly useful for specialized applications.

The best results were obtained with a polysulfide liquid polymer, LP-3, in which the powders were dispersed. The mixture was injected into the delay bodies and the polymer was converted to an elastic rubber by heating to 170°F. A small quantity of sodium tetraborate decahydrate was used as the curing agent. It releases its water of hydration at about 170°F to initiate the cure. This injection system for filling the bodies with delay mixtures can be readily adapted to quantity production. It also may make it possible to make delay compositions in unusual shapes that could not be loaded with dry powder.

Tests<sup>(13)</sup> showed that these compositions would burn in a 5/32 in. column at -70°F, and that storage for 3 months at 170°F had very little effect on the burning time. The burning time of T6E3 units loaded with one of these compositions is shown below. Unfortunately, the number of units tested and the standard deviations are not available.

Table VI. Burning Time of Castable Delay Composition

Temp (F°)	Burning Time (sec) in T6E3 Delay Units		
	Av	Min	Max
-70	15.65	13.78	16.43
80	13.10	12.59	15.75
170	13.03	12.11	14.01

The burning time of these compositions was shown to be almost independent of pressure from 30 to 2100 psia. This characteristic may allow the delay composition to be ignited directly from burning propellant in a mortar fuze or rocket motor, since the high propellant gas pressure would not affect the burning time of the delay.

No further development of these compositions is recommended unless required for specific end items.

## 7. CALORIMETRY

The burning rates of gasless delays vary with the ambient temperature, but it is not known whether this is caused by a change only in the reaction rate or by a variation in the heat evolved by the reaction. Methods<sup>(1,41, 42,43,44,45,46)</sup> have been developed for measuring the heat evolved by

thermite mixtures but these were developed for heat source application and are not applicable to delay studies.

Therefore, a microcalorimeter<sup>(46,47)</sup> was developed for measuring the heat (100 to 300 cal) evolved by small quantities of gasless mixtures at any ambient temperature within the range  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ . This instrument consists of a copper block bomb, a thermistor temperature measuring bridge circuit, a suspension platform, a vacuum housing, a dead air chamber, and a constant temperature chamber. In its present form the apparatus will be most useful in research applications. Each run requires several hours because of experimental difficulties and the time required for temperature equilibrium.

Tests were made at  $-65^{\circ}\text{F}$ ,  $+71^{\circ}\text{F}$  and  $+165^{\circ}\text{F}$ , using heat mixtures during calibration and evaluation tests. However, time did not permit evaluation of the delay mixtures as originally intended.

This instrument appears adequate for these types of investigations and no further development is recommended.

#### 8. GAS EVOLUTION

An apparatus<sup>(18,48)</sup> was developed for measuring the small quantities of gases evolved by heat and delay mixtures. The apparatus consisted of a modified calorimeter bomb equipped with a strain-gauge pressure transducer; a simple electrical circuit for direct reading of the pressure, and for calibration; and a salt bath maintained at  $135^{\circ}\text{C}$ . Readings taken at  $135^{\circ}\text{C}$  and at room temperature allowed the determination of condensable and noncondensable gas as well as total gas. The sensitivity of the method is 0.01 ml of gas for the usual sample weighing 2g, or 0.005 ml/g. About 30 min is required for a determination.

This apparatus appears to be satisfactory for both development and control purposes and no further development is recommended.

#### 9. MIXING

An agglomerate mixing method<sup>(7,15,16,18)</sup> was developed for blending small particles into homogeneous pyrotechnic mixtures. This procedure has been found particularly useful for blending fast burning zirconium-barium chromate compositions. The uniformity of blending is illustrated by the burning times obtained with a typical mixture loaded and tested in 20 T2E1 delay elements. The burning times were within  $39.56 \pm 1.76$  ms calculated for 95 percent of all future observations at a 90 percent confidence level. The reproducibility of the burning characteristics of successive batches is shown in table I.

This method has not been used to any extent for blending slow burning mixtures. The particle sizes of manganese powder generally used in manganese delay composition are too large for this blending procedure and

the particles do not form agglomerates. Tests showed that tungsten delay compositions prepared by agglomerate blending did not burn evenly although the mixtures appeared to be well blended by microscopic observation. Later work showed that the uneven burning times could be eliminated by using a very short dry mixing procedure and a split igniter. Very possibly, the agglomerate mixes could have been prepared to burn evenly with a split igniter but no further tests were made since the wet mixing method required dispersing the mix, which included potassium perchlorate, in a flammable solvent.

The agglomerate method is a wet mixing procedure developed specifically for producing homogeneous pyrotechnic mixtures. A suspending fluid must be used in which the particles do not disperse but form agglomerates naturally. This agglomerating tendency must persist after the mixture is dried, as well as while the components are being blended. The agglomerates that generally are formed are about 20  $\mu$  in diameter and, therefore, the particles should be well below this size, about 1 to 5  $\mu$  in diameter. The mixing is accomplished by mechanical methods including ball mills, colloid mills, and high-speed kitchen blenders. Each of these produces liquid shearing forces that break agglomerates into individual particles and allow them to mix. As soon as the particles move out of the region of fluid shear, they immediately reagglomerate and act as particles of the mixture, not as individual components. There is no tendency for the components to segregate and the weight ratio of the components in each agglomerate remains constant throughout subsequent handling operations.

This mixing procedure appears to be adequate and no further mixing investigation is recommended.

## 10. NEW METHODS

### 10.1 Flat Pyrotechnic Material

One method that has been suggested<sup>(8)</sup> for producing controlled time delays with pyrotechnic mixtures is to make the mixture in a flat form similar to that used for heat source material. With this procedure the delay mixtures could be formed into spiral and other compact shapes that could not be made using conventional dry powder loading techniques.

An accurate burning rate tester was constructed<sup>(49)</sup> and a number of tests were made with fast burning material to evaluate the instrument. Although the burning rate tester was completely satisfactory, the burning times of the flat material were not very uniform. No further tests were made with slower burning compositions, since there did not appear to be any end-item requirement for this type of material.

It is recommended that no further work be done unless there are specific requirements for this type of material.

## 10.2 Thermal Delay

A thermal delay consists of a heat source, a heat barrier, and a heat-sensitive chemical on the opposite side of the barrier from the source. The barrier may vary in shape and composition from a long rod of metal to a very short disc of ceramic. The heat-sensitive chemical may be an explosive or a solid nonconductive material that melts and becomes conductive when heated to a definite temperature.

Although thermal delays have been considered<sup>(9,10,11,12)</sup> since 1950, the only delays of this type to be produced in quantity are found in the T-1012 fuze<sup>(50)</sup>. The earlier proposal<sup>(9)</sup> suggested melting solder or other metals to keep the thermal delay heater constant and to overcome ambient temperature effects. The same principle was used in the experimental fuze described in reference 51. The T-1012 fuze already had a heat source that operated near a constant temperature, and the thermal delay was added to this.

The Physics Department of the Virginia Military Institute was asked to investigate the factors influencing the design of a thermal delay and to determine the optimum functioning times that might be expected from such a device. Their investigation<sup>(11)</sup> was divided into two parts. The first considered the minimum diameter of a pyrotechnic heater that would operate for a given time at a fixed temperature irrespective of ambient temperature when the latter varied between  $-65^{\circ}\text{F}$  and  $+165^{\circ}\text{F}$ . This device was considered to be a series of cylinders with  $\text{Zr-BaCrO}_4$  heat powder in the center surrounded by a cylinder of fusible material contained in another cylinder of steel. The whole device was then contained in another cylinder of ceramic. Under these conditions, a device 3.5 cm in diameter containing solder melting at  $188^{\circ}\text{C}$  would hold its temperature for 10 sec. A similar device 2.8 cm in diameter containing zinc would hold its temperature at  $419^{\circ}\text{C}$  for 10 sec. If the time were extended to 150 sec using zinc, the diameter required would be 8.7 cm. Each time the large diameter was required by the heat losses, and if a better insulator could be found the diameter could be reduced considerably. For example, a device only 1.5 cm in diameter theoretically could maintain its temperature at  $419^{\circ}\text{C}$  for 150 sec if air could be used as an insulator. Obviously, some support would be needed but the support might be limited to the ends of the cylinder, thus reducing the heat losses. The minimum diameters were calculated assuming an infinite length. In an actual device the length probably would be about 1.5 or 2 in. including the electric initiator that would be required.

Calculations, and actual tests, have shown that a cone produces lower time dispersions than a rod over the military ambient temperature range. However, under the best conditions when one end of the cone is held at a constant temperature the time dispersion will be at least  $\pm 5$  percent and probably much more.

The thermal delay appears best suited to applications where a constant temperature source already exists and no other constant temperature heat source is necessary. It is recommended that no further work be done unless required by specific applications.

## 11. CONCLUSIONS AND RECOMMENDATIONS

The advantages of pyrotechnic delays are operation over the temperature range  $-100^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ , operation under very high impact forces, relatively low cost, and small size. Over the ambient temperature range  $-35^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ , and under optimum conditions, the times of delays burning within 20 sec will vary about  $\pm 12$  to 13 percent. When the delays are longer or when the conditions are less favorable, the burning time dispersions may increase to twice this value. New methods suggested for employing pyrotechnic mixtures appear to offer no advantages over present methods unless used for specialized applications.

The present compositions appear to be satisfactory for current DOFL requirements and no further investigations are recommended.

## 12. REFERENCES

- (1) DOFL Technical Report No. TR-884, "Pyrotechnic Research at DOFL. Part 1. Heat Source Materials," Raymond H. Comyn, 28 November 1960 (C).
- (2) DOFL Technical Report No. TR-346, "Development of T2E1 Pyrotechnic Delay Element. Part I. Zirconium-Barium Chromate Delay Compositions," James D. Yancey, Jr. and Richard H. Weingard, 1 June 1956 (U)
- (3) Design Release Data—T2E1 Delay and Non-Delay, James D. Yancey, Jr., and Richard H. Weingard, March 1955 (U)
- (4) Design Release Data—T3E4 Delay Element, Raymond H. Comyn, December 1956 (C)
- (5) DOFL Technical Report No. R320-61-16, "Engineering Test Data. T5E3 Delay Element," N. Martin, September 1961 (U).
- (6) "Design and Development of 7 and 60 Second Delay Switch," Progress Reports, Universal Match Corp, Armament Division, Explosives R&D Laboratory, Crab Orchard Plant (Sandia Corp Purchase Order 14-69-22), 1958 (C).
- (7) DOFL Report No. R22-57-6, "The Use of Gasless Mixtures for Producing Time Delays in Ordnance Devices," Raymond H. Comyn, 16 October 1957 (C).
- (8) DOFL Technical Memorandum No. TM-605, "The Use of Chemical Reactions in S&A Devices," Raymond H. Comyn, 11 February 1960 (U)
- (9) Memorandum to NOL Files, "Thermal Delay Pyrotechnic Heater," Raymond H. Comyn, October 1950 (U).
- (10) NOLM 10378, "Basic Radiant Heat Transfer Test to Determine the Feasibility of Application to Thermal Delay Units," H. Martin, September 1951 (U).
- (11) Report 869-3 Part I. "Thermal Delays Constant Temperature Heat Source," Part II. "Temperature vs Time in Heat Conductors," Virginia Military Institute, Dept of Physics, September 1961 (U).

- (12) Supplement to Final Summary Report, Contract DA-49-186-502-ORD-473, prepared by Zenith Radio Corporation for DOFL, June 1958 (C).
- (13) "Development of Improved Loading Methods for T-6 Type Delay Elements," Summary Report Contract DA-I-49-186-502-ORD-P362, prepared by Thiokol Chemical Corporation, Elkton, Maryland for DOFL, September 1956 (C).
- (14) DOFL Report R450-61-21, "Summary of Pyrotechnic Delay Investigations for the AEC and the Sandia Corp" (Purchase Order AEC AL-58-943, Sandia Corp. ASB-14-9986,) Raymond H. Comyn, September 1961.(U)
- (15) DOFL Technical Report No. TR-635, "Specification of Barium Chromate for Use in Gasless Mixtures," Raymond H. Comyn, Mardelle L. Couch, and Robert E. McIntyre, 17 September 1958.(U)
- (16) DOFL Technical Report No. TR-648, "Factors Affecting the Blending of Gasless Mixtures," Robert E. McIntyre, 24 February 1959 (C).
- (17) DOFL Technical Report No. TR-821, "Specification of Zirconium for Use in Gasless Mixtures," Robert E. McIntyre and Mardelle L. Couch, 9 March 1960 (U).
- (18) I & E Chem Vol 52, p 995, December 1960, "Agglomerate Mixing," Raymond H. Comyn, Ira R. Marcus, and Robert E. McIntyre.
- (19) X-TL-PD-15, "Proposed Purchase Description. Delay Element, T6E4 and T5E3," 18 October 1956 (C)
- (20) X-TL-PD-16, "Proposed Purchase Description. Igniter Composition DM-5," 18 October 1956 (C)
- (21) X-TL-PD-17, "Proposed Purchase Description. Delay Composition DM-4," 18 October 1956 (C)
- (22) Navord Report 1787, "Effect of Pressure on the Burning Rate of Gasless Delays," Raymond H. Comyn and R. Skelton, 17 February 1951 (C).
- (23) DOFL Report No. R320-61-17, "M42G Primer Study," Robert E. McIntyre, June 1961(U)
- (24) DOFL Technical Report No. TR-965, "Stability of Manganese Delay Mixtures," Raymond H. Comyn, Mardelle L. Couch, and Robert E. McIntyre, November 1961 (U).
- (25) Navord OS8976A, "Descriptions and Requirements, Powders, Ignition, Gasless," 12 March 1959 (U).
- (26) DOFL Technical Report No. TR-875, "Development of a Split Igniter for Initiating Gasless Delays," Ira R. Marcus, 14 November 1960.



(27) DOFL Technical Report No. TR-495, "Determination of Gases in Barium Chromate for Use in Pyrotechnic Delay and Heat Mixtures," Mardelle Couch, 1 June 1957 (U).

(28) DOFL Technical Report No. TR-636, "Measurements of Particle Size of Components of Gasless Mixtures," Raymond H. Comyn, Mardelle L. Couch, and Robert E. McIntyre, 28 August 1958 (U)

(29) Navord Report 1775, "Manganese and Cobalt Delay Mixtures," Raymond H. Comyn and R. Skelton, 30 March 1951 (C)

(30) Navord Report 1814, "A Method of Protecting Metal Powders from Deterioration," Raymond H. Comyn and R. Skelton, 18 April 1951 (C).

(31) Navord Report 2261, "Burning Characteristics of Manganese, Barium Chromate, and Lead Chromate Mixtures," E. E. Elzufon, 17 January 1952 (C).

(32) Navord Report 2262, "Effect of Loading Variables on the Burning Characteristics of Delay Powders," E. E. Elzufon, 19 December 1951 (C).

(33) BuOrd Dwg. No. 1183355 NOL D-16 "Delay Powder: Requirements and Test Procedures" (C).

(34) Navord OD-9360, "Preparation of Manganese Delay Composition," Second Revision, 17 January 1958 (U)

(35) "Fuze Explosive Trains. Summary Report No. 2," Contract Nord 13466 Task 2, Universal Match Corp., 12 May 1958 (C).

(36) OS-11131 "Descriptions and Requirements, Tungsten Delay Composition," 1 December 1960 (U)

(37) DOFL Report R320-61-20, "Investigation of Component and Process Variation for Tungsten Delay Compositions," Robert E. McIntyre, September 1961 (U)

(38) DOFL Progress Report on Dev. Contract AEC AL-58-943, June 30 1958 (C)

(39) DOFL Report R320-61-2, "Investigation of Environmental Effects on Tungsten Delay Compositions," Norman L. Martin, 17 January 1961.

(40) DOFL Report R450-61-22, "Investigation of the Effect of Delay Body Variables on the Burning Characteristics of Tungsten Delay Compositions," Raymond H. Comyn and Robert E. McIntyre, October 1961.

(41) DOFL Technical Report No. TR-488, "Measurement of Heat Evolved by Thermite Mixtures, Part I. The Design and Calibration of a Calorimeter for Use as a Primary Standard," John P. Gibbons, March 1957 (U)

(42) DOFL Technical Report No. TR-494, "Measurement of Heat Evolved by Thermite Mixtures. Part II. Factors Affecting the Heat Evolved by Thermite Reactions During Calorimetric Measurements," John P. Gibbons, March 1957 (U)

- (43) DOFL Technical Report No. TR-576, "Measurement of Heat Evolved by Thermite Mixtures. Part III. Standard Calorimetry for Quality Control," Ira R. Marcus, 15 January 1958 (U).
- (44) DOFL Report No. R22-57-8, "The Use of the Parr Peroxide Bomb Calorimeter for Measuring Heats Evolved by Thermite Reactions," Thomas C. Boberg, 6 November 1957 (U).
- (45) DOFL Report No. R320-59-12, "Calibration of the Parr No. 1411 Heat Powder Calorimeter," Mardelle L. Couch and Ira R. Marcus, 16 December 1959 (U).
- (46) DOFL Technical Report No. TR-862, "Summary of Heat Powder Calorimetry," Raymond H. Comyn and Ira R. Marcus, 1 August 1960 (C).
- (47) DOFL Technical Report No. TR-844, "Measurement of Heat Evolved by Thermite Mixtures. Part IV. A Laboratory Microcalorimeter for Evaluating Thermite Mixes from -65°F to +165°F," Ira R. Marcus, 20 June 1960 (U).
- (48) DOFL Technical Report No. TR-702, "Procedure for Determination of Gas Evolved by Thermite Mixtures," Robert E. McIntyre, 4 February 1960 (U).
- (49) DOFL Technical Report No. TR-846, "Burning Rate Tester," Ira R. Marcus, 25 July 1960 (C).
- (50) DOFL Technical Report No. TR-649, "T-1012 Electric Impact and Time Fuze for Hand Grenade," L. Richmond, March 1959 (C).
- (51) DOFL Technical Report No. TR-673, "Octopus Fuze T362," 10 August 1959 (C).

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